Modelling the effect of hydrogen positions on the lattice dynamics calculations of terahertz spectra of benzoic acid

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***Abstract*— Using the known crystal structure of benzoic acid, the impact of hydrogen disorder on the phonon modes and terahertz spectrum is systematically evaluated using computationally inexpensive rigid molecule atomistic lattice dynamics calculations. The predictions are compared to the measured terahertz spectra.**

I. INTRODUCTION AND BACKGROUND

WITH the rapidly growing number of experimental activities using terahertz time-domain spectroscopy (THz-TDS) to study organic molecular crystals, there is a demand for accurate assignments of the observed vibrational modes at terahertz frequencies. A number of approaches have been developed to calculate terahertz spectra, including lattice dynamics based on atom-atom model potentials[1-2] and on periodic electronic structure theory.[3-4] However, there have been few systematic studies to explore the best computational strategy for the assignment of the features in terahertz spectra. A major limiting factor for such systematic studies is the computational cost associated with full electronic structure lattice dynamics calculations under periodic boundary conditions. We have therefore explored the use of computationally less demanding atom-atom model potential calculations.

We use benzoic acid as a model system for our calculations, as the molecule is rigid and high quality crystal structures of the compound have been determined from neutron diffraction at several temperatures from 20-175 K.[5] Benzoic acid molecules form hydrogen bonded dimers in the crystal structure, with pairs of hydrogen bonds between carboxylic acid groups (Fig.1, right). The experimental studies show that the hydrogen atom position is disordered over two sites in these dimers and, in this study, we have systematically evaluated the influence of the hydrogen position within the acid dimers on the simulated spectra from lattice dynamics calculations in the atom-atom approach. Rigid molecule harmonic lattice dynamics calculations were performed as described elsewhere,[1-2] using the crystal structure modeling program DMAREL, which allows an accurate representation of intermolecular electrostatic interactions via a distributed multipole model. Results of the simulations are validated against experimental THz-TDS spectra obtained at 110 K and 300 K. Furthermore, we visualized the dimer distortions from the eigenvector associated with each calculated lattice mode and classified the modes according to the different types of hydrogen bond distortion, which include: in-plane bend; out-of-plane bend and twist (Fig. 2). Only these dimer distortions, which break the inversion symmetry of the dimers and generate a dipole moment in the unit cell, result in features in the terahertz spectrum.

II. RESULTS AND DISCUSSIONS

Lattice dynamics calculations were performed using two ordered models of the crystal structure, with each of the two hydrogen atom positions, which we label according to the oxygen atom (O_α or O_β) to which the hydrogen is bonded. The resulting spectra, assuming a Lorentzian peak shape, are shown in Fig. 1 (lower two traces), along with the observed room temperature and 110 K THz-TDS spectra (upper two traces). The only differences in geometric models are the hydrogen site and associated relaxation of the acid group carbon-oxygen bondlengths, but this small structural change has a dramatic effect on the resulting vibrational modes (shown without the assumed peak shape in Fig. 3). There is a preferred agreement between the O_β model (second trace from bottom in the Fig.1) and the low temperature observed spectrum, with an overall shift to higher frequency in the simulated spectrum. This observation is in agreement with the observed low temperature hydrogen site occupancies, which show that the O_β site is more highly occupied (0.33:0.67 for sites O_α:O_β at T = 100 K).[5]

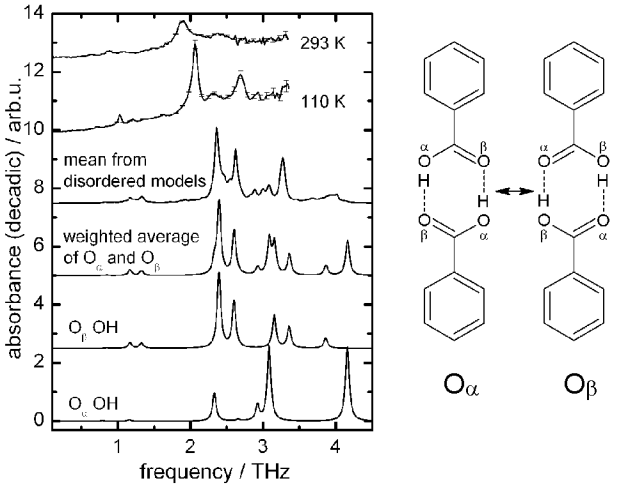

Figure 1. Measured terahertz spectra of benzoic acid, and simulations with various models for the hydrogen atom positions and associated disorder.

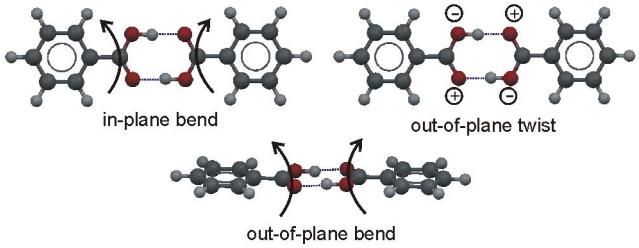

Figure 2. Types of distortion of the hydrogen bond dimer.

We have also investigated models for the terahertz spectrum of the disordered benzoic acid crystal. A first approximation is the weighted average of the calculated spectra from the O_α and O_β ordered models (third trace from bottom, Fig. 1), which would be expected if extended domains of each configuration are present in the crystal structure. The alternative is that O_α and O_β dimers are distributed randomly throughout the crystal. To model this case, the crystal structure was expanded into a

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supercell containing 24 molecules (12 dimers) in which 4 random dimers were created with the O_α molecular geometry, while the remaining 8 dimers had the O_β molecular geometry. Four such random models were created and the lattice dynamics calculations were performed on each. The average spectrum from these disordered models is shown in Figure 1 and shows the best agreement with the 110 K measured spectrum of all of the calculated models. Therefore, we believe that the terahertz spectrum is providing useful information on the nature of the disorder in the benzoic acid crystal structure.

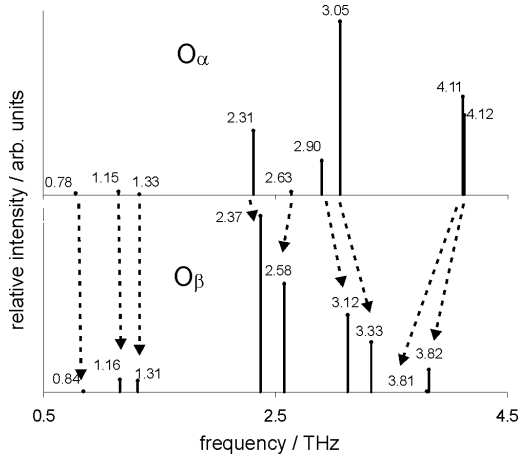

Figure 3. Calculated harmonic vibrational modes with the two ordered models of the benzoic acid crystal structure.

Mode		Freq./ THz	Relative Intensity	Corresponding Dimer Distortions
1	Oα	0.779	0.004	slight in-plane bend + slight out-of-plane bend
	Oβ	0.843	0.003	slight in-plane bend + slight out-of-plane bend
2	Oα	1.147	0.009	out-of-plane bend + slight twist
	Oβ	1.158	0.035	out-of-plane bend + slight twist
3	Oα	1.326	0.002	out-of-plane bend + slight twist
	Oβ	1.312	0.032	out-of-plane bend + slight twist
4	Oα	2.309	0.174	large out-of-plane bend + in-plane bend + slight twist
	Oβ	2.372	0.479	large out-of-plane bend + in-plane bend
5	Oα	2.634	0.009	large out-of-plane bend + in-plane bend + slight twist
	Oβ	2.577	0.294	large out-of-plane bend + slight in-plane bend
6	Oα	2.897	0.093	large in-plane bend + out-of-plane bend
	Oβ	3.124	0.210	large in-plane bend + out-of-plane bend
7	Oα	3.054	0.470	large in-plane bend + out-of-plane bend + slight twist
	Oβ	3.327	0.136	large in-plane bend + out-of-plane bend
8	Oα	4.112	0.266	large out-of-plane twist
	Oβ	3.823	0.062	large out-of-plane twist
9	Oα	4.124	0.216	large out-of-plane twist
	Oβ	3.807	0.003	large out-of-plane twist

Table 1. Descriptions of the calculated vibrational modes in the two ordered models of the benzoic acid crystal structure.

To get an understanding of the nature of the individual lattice vibrations, the eigenvectors from the two ordered models were visualized and classified according to the type of hydrogen bond dimer distortion caused by the lattice mode (Table 1 and Fig. 2). Each mode is expressed as an eigenvector describing the translation and rotation of the molecules. The components of these eigenvectors were compared to correlate the vibrational modes in the two ordered models of the crystal structure. The modes with similar eigenvectors in the two models of hydrogen sites are associated with the same type of dimer distortion, with only small differences in molecular motion. Together with the visual comparison of the vibrational modes, the vibrations with similar dimer distortion are indicated in Fig. 3 and details of the corresponding combinations of symmetry breaking dimer vibrations are listed in Table 1.

From this analysis, we notice that the types of vibration in both crystal models changes from out-of-plane bending at low frequencies, to in-plane-bending motions in the middle of the spectrum and the highest frequency modes are largely those that twist the hydrogen bonded dimers. The relative absorption intensity is very dependent on the position of the hydrogen atoms in the dimer: the out-of-plane bending modes have a greater intensity in the O_β model than in the O_α model, while the relative intensities of the in-plane bending and twisting modes decrease significantly in the O_β model. Finally, we find that the frequency shift of out-of-plane bend dominated modes between the two models are fairly small and random, while the in-plane bend and twist dominated modes show shifts as large as 0.3 THz: in-plane bending modes shift to higher frequencies and twisting modes shift to lower frequencies in the O_β model.

III. CONCLUSIONS

The results demonstrate the usefulness of the rigid-molecule atom-atom model potential for efficiently exploring the influence of molecular structure and disorder on the lattice dynamics in molecular crystals, helping characterize measured terahertz spectra. We find a strong dependence of the calculated spectra on the position of the hydrogen atom in the hydrogen bond dimers, which has provided information on the nature of the disorder in the crystal structure.

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